A STUDY OF THE COLORING EFFECTS OF SMALL AMOUNTS OF RARE EARTH OXIDES ON FUSED ALUMINA AND SILICA

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A STUDY OF THE COLORING EFFECTS OF SMALL AMOUNTS OF RARE EARTH OXIDES UPON FUSED ALUMINA AND SILICA

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From earliest ages man has admired and coveted the beautiful precious stones which nature has given to us. Many have tried to imitate them, and a few attempts have been made to produce these precious stones synthetically. Imitations can always be detected, and synthesizing has met with success in only two cases. Moissan has made microscopic diamonds. Verneuill has successfully produced large size rubies. These rubies are identical with natural rubies in all their physical and optical properties, with one exception. This difference is that synthetic rubies contain a variable number of spherical gas bubbles of microscopic size, while any inclusion of foreign matter in the natural ruby has followed the lines of flow and hence is longitudinally striated. The difference does not detract from the value or usefulness of the synthetic ruby and may only be detected by special optical instruments.

The present work was undertaken to make synthetic rubies and silica gems, then to study the theory that the colors in our precious stones are due to small amounts of rare earth oxides.

Procedure

Verneuill's method of introducing a very finely divided mixture of ammonium alum and chrom-ammonium alum into the oxy-hydrogen blow-pipe flame produces rubies which can only be differentiated from natural rubies in the manner described above. Hoping to avoid

this trouble of included gas bubbles, the fusions were made in an Arsem Vacuum Furnace of the A-1 type. Instead of using the alums, pure alumina was prepared from ammonium alum beforehand. Weighed amounts of alumina or silica and of the coloring constituent to be used were ground together in a smooth stone mortar. This well ground material was placed in the furnace in a crucible. The furnace was sealed, evacuated and then heated to the required temperature. The cooling required one to two hours time, after which the vacuum could be released. The observation tube was then removed, and the crucible, containing the fused charge, was withdrawn and inspected.

Apparatus

The furnace: The furnace used was an Arsem Vacuum furnace of the A-1 type, i. e. the small vertical type, which has a heating element about 6 in. long, supported in an upright position. This heating element is a graphite resistance sector, which is made in the form of a helix. It is supported at both ends by the electrode leads, which are made of seamless brass tubing. Water, flowing through these tubes and around the outer shell, serves to keep the leads and container cool. The helix is surrounded by a hollow cylinder of graphite filled with graphite powder. This cylinder acts as a radiation screen and increases greatly the heating efficiency of the furnace. The crucible is placed on a pedestal, which arises from the bottom support within the helix. This whole arrangement is secured to a heavy stell plate properly insulated, and bolted in place within a steel tank, which forms the outer shell. For further details of the furnace see the bibliography and Fig. 1.

The Construction of a Heating Element: The helix is made from a piece of Acheson graphite 12" long and $2\frac{1}{2}$" in diameter. Mark the end centers on a centering lathe. Then chuck a 1-5/8" twist drill in a lathe; put the lathe on slow speed and feed the piece of graphite against the drill by hand pressure. Feed slowly and keep a firm pressure. Do not let the piece wobble, or the hole will not be true. It will be necessary to drill from both ends unless an exceptionally long drill is to be had. Mount the cylinder, obtained in this manner, upon a wooden mandrel. Then turn down in a lathe at moderate speed to the dimensions given in the drawing, Fig. 2. Then adjust the spiral gear cutter to give 2/3 of a turn to the inch and cut the thread. Use very slow speed (the back-gears), and take only a small cut each time. See the diagram (Fig. 2) for width of thread and spacing from the ends. Do not cut the thread completely through, but nearly so. Then slip the tube from the mandrel. Next place it upon a perfectly flat surface and carefully finish cutting the spiral with a hack saw blade held in the hand. Fit the ends of the helix to the holding cup by brushing down with fine sandpaper. It is now ready to put in place in the furnace. See Fig. 1.

Evacuation: The evacuation is accomplished by means of a Geryck Oil Pump connected to the furnace cylinder by heavy pressure tubing. The line is connected to a monometer to determine when evacuation is complete. There is also in the line, a by-pass valve for the purpose of releasing the vacuum or admitting any inert gas to the furnace cylinder. The rubber tubing and ordinary glass-stoppered valves prove quite satisfactory on the vacuum line. The leakage in 24 hours changes the manometer reading by 6mm.

Heating and Controlling Apparatus: The heating is accomplished

by means of a 15 K. W. transformer. The primary voltage is 220 Volts. The voltage is in steps of 10 volts from 10 to 60 on the secondary. In order to control the voltage between these points, two graphite block resistances of the pressure type and an A. C. ammeter (0-75) are used in series with the primary. This control group may be shunted by closing a heavy switch.

Measurement of Temperature: The temperature may be read in either one of two ways. (1) The temperature input-curve is obtained for the furnace by melting copper, platinum and iridium. A 400 to 5 current transformer is connected to one of the feed wires and an ammeter (A. C. 0-5) is connected across it. A 0-30-60 voltmeter is connected directly across the terminals of the furnace. See fig. 4. The metals are placed within the furnace and the temperature slowly raised. As each metal softens and melts down the readings on the meters are recorded and from these the power-input in K. W. can be calculated and plotted against the melting point for each metal. A smooth curve is drawn through these points and from this curve the temperature at any future time may be read by measuring the input. (Note: It is necessary in this method that the temperature of the crucible be, as nearly as possible, the same as that of the helix. (2) The other method of reading the temperature is to use directly an optical pyrometer. The one used was a Leeds and Northrup and gave very good checks with the temperatures determined from the power curve. It checked within 25° below temperatures of 1800° C, and within 50° for temperatures around 2000° C. For graphs of these methods see Figs. 5 and 6 respectively.

Materials

Al_2O_3: Prepared by ignition from Mallinckrodt's c.p.$NH_4Al(SO_4)_2$

Cr_2O_3: Prepared by ignition from Mallinckrodt's c.p.$NH_4Cr(SO_4)_2$

SiO_2 : This material analyzed 98% SiO_2 and when fused alone gave a clear silica bead. It was therefore considered pure enough for the work to be undertaken.

CeO: Prepared from 98% $Ce(NO_3)_2$ by ignition.

MgO: Baker's analyzed C. P.

Nd_2O_3: Obtained from rare earths laboratory 90-95% purity.

TiO_2 : Obtained from rare earths laboratory, 97% purity.

Experimental

Selection of a Crucible: Graphite: In a small piece of Acheson graphite, one inch in diameter and one inch long, a hole one-half inch in diameter was drilled to a like depth. The alumina mixture was placed in this crucible and fired in the furnace to fusion. The fused mass when examined showed just enough finely divided graphite to give it a dirty color. Upon using this crucible a second time the amount of graphite included in the fusion was less. This amount gradually diminished with repeated use, but never became negligible.

CaO: Next a small chunk of Cao was shaped into a crucible by means of a knife and drill. This crucible was fired to 2300° C in order to shrink it. After shrinkage, which was very little, it was charged with a mixture of alumina and placed within the furnace. When a temperature of 1800° C had been obtained, the alumina reacted with the CaO and fused down into it, eating a hole right through the CaO. Therefore, CaO as a crucible was out of the question.

Molybdenum: Next a small dish of pure molybdenum was turned

out on a lathe and filled with a charge. The crucible was placed in the furnace, being as careful as possible to insulate it from any graphite, for molybdenum carbide forms and melts at a temperature of about 1750° C, while molybdenum melts at 2535° C. MgO was used as an insulator, but no cover was placed over the dish. Upon heating, some small particles of graphite disintegrated from the helix and dropped into the dish. When a temperature of 1800° C was reached, the dish melted. The use of molybdenum was then an impossibility, unless a means could be devised to perfectly insulate it from all graphite.

It was then decided to use graphite crucibles which had been fired several times.

Results

No.	Mixture	Temp.	Color	Memoranda	Atmosphere
1	Al_2O_3:3%Cr_2O_3	2000° C	Pink-red	Bubbly	Vacuum
2	" 5% "	"	Deep ruby	"	"
3	" 3% "	"	White	Crystals	Nitrogen
4	SiO_2:0.5% "	1750°C	Azure blue	Sl.bubbly	Vacuum
5	" 1% "	"	Blue-green	bubbly	"
6	" 2% "	"	Dirty green	"	"
7	Al_2O_3:1% CeO	2000° C	No color	Sl.bubbly	"
8	" 8% "	"	"	"	"
9	SiO_2:1% CeO	1750° C	Milky, Opalescent in spots.		"
10	" :3% "	"	More densely opalescent (bubbly)		"
11	" :8% "	"	Opaque	Bubbly	"
12	" :Ce_2O_3	1800°C	Brown-black lustreless (No bubbles)		"
13	Al_2O_3:1%Nd_2O_3	2000°C	No color	Bubbly	"
14	" :4% "	"	No color	Bubbly	V
15	SiO_2:1%Nd_2O_3	1750°C	Faint Pink-lavender tint Opalescent	Bubbly	"

16	SiO_2:4% Nd_2O_3	1750°C	Faint Pink-lavender more densely opalescent (bub)	Vacuum
17	" :8% "	"	Same color Opaque Bubbly	"
18	SiO_2:5%FeO;3%CaO	"	Black flint color No bubbles	"
19	Al_2O_3:5% TiO_2	1900°C	Material sparked and flashed violently	"

Discussion

Nos. 1 & 2 gave a synthetic ruby which differed from the natural in that it was filled with a mass of minute bubbles. This mass of bubbles could be removed by heating to a little above the fusion temperature and cooling very carefully. But in doing so all color was lost in alumina fusions, while in silica fusions the color was retained.

No. 3 was carried on in an atmosphere of nitrogen to eliminate the bubbles which were thought to be due to the vaporizing of the alumina itself. Instead of fusing, the alumina reacted with the nitrogen and gave in the bottom of the crucible a growth of white fine needle-like crystals. These crystals have been exposed to aire for eight weeks and are perfectly stable. A test was made for nitrogen which was found present. It was thought that this might be some form of aluminum nitride. Some tests were made but the results were neither positive nor negative. Nitrogen was used with silica fusions but did not reduce the bubbles so the process was continued in vacuo.

Nos. 4, 5, & 6 gave some very interesting results with silica and chromium oxide. The No. 4 fusion would be quite pretty if it were possible to eliminate all the bubbles.

Nos. 7, 8, 13 and 14 showed that CeO and Nd_2O_3 have no effect on alumina.

Nos. 9, 10, & 11 indicated that CeO has no coloring effect upon silica, but produces instead an opalescent effect upon the

surface, when used in very small amounts.

No. 12 was an attempt to form a cerium cilicate by fusion. The mass obtained was not analyzed.

Nos. 15, 16 & 17 indicated that Nd_2O_3 faintly colors silica, and produces an opalescence, when used in very small amounts. In larger amounts, as in the case of CeO, the mass becomes opaque. This leads one to believe that possibly all of the rare earth oxides, being quite heavy, would produce the same effect.

No. 18 looked very much like real flint and was as hard.

No. 19 is discussed in the notes.

Notes

During this work the melting points of some refractories were determined which compare with American and German literature in the following manner.

Substance	M. P. Observed	American	German
MgO	2500° C	1800°- 2000°	2800°
CaO	2300° C	1950° C	2500°
SrO	2000° C	3000° C	White Heat

It was observed that it was necessary to heat Al_2O_3 very gradually up to a temperature of 800° C to prevent the Al2O3 from violently hopping about and out of the crucible. This effect was first noticed with alumina formed by decomposing the ammonium alum over a Meker burner, and it was thought possible that it might not have been completely decomposed. Therefore, some of the alumina was fired in a muffle furnace to a temperature of 1200° C. Upon using this material the effect was the same, when heated rapidly in an atmosphere of nitrogen and no such hopping about would occur. This leads to a possiblitly of two conclusions.

The first and more probable is, that due to the helix form of the heating element, the hopping about is caused by magnetic effects upon alumina. The other possibility is that the alumina has adsorbed moisture so that when heated rapidly in vacuo it jumps about because of the rapid loss of this moisture, where as it would not lose this moisture so rapidly in an atmosphere of nitrogen at normal pressure. There is one piece of evidence which substantiates the first theory. If a smooth bottom graphite crucible is placed in the furnace on a support with a smooth top, and heated to a temperature of 2100° C, this crucible, after being held at this temperature for a short time, will slide across the pedestal until it touches the helix. Also a molten charge of either silica or alumina will whirl around within the crucible, in the direction of the spiral cut of the helix.

It was observed in the case of alumina and the rare earth oxides that at a temperature just below the fusion point there was considerable sparking and flashing. This was so vigorous in case of TiO_2 (No. 19) that all the charge was exploded from the crucible. It may be this same manner of loss is the cause of the lack of color in the alumina fusions with CeO and Nd_2O_3.

Conclusions

1. Molybdenum would make the most suitable crucible, if it be perfectly insulated from all graphite.

2. Alumina fused with a small amount of Cr_2O_3 gives a product which has the color and hardness of a natural ruby.

3. The depth of color imparted to the alumina is a function of the amount of Cr_2O_3 added.

4. The oxides CeO and Nd_2O_3 in the proportions and manner used are unsuitable for the purpose of coloring either fused

alumina or silica.

5. The difference between the action of Cr_2O_3 upon fused alumina and fused silica, upon continued heating, may lead to some light upon the state in which the Cr or Cr_2O_3 is combined with the Al_2O_3 in the ruby.

Bibliography

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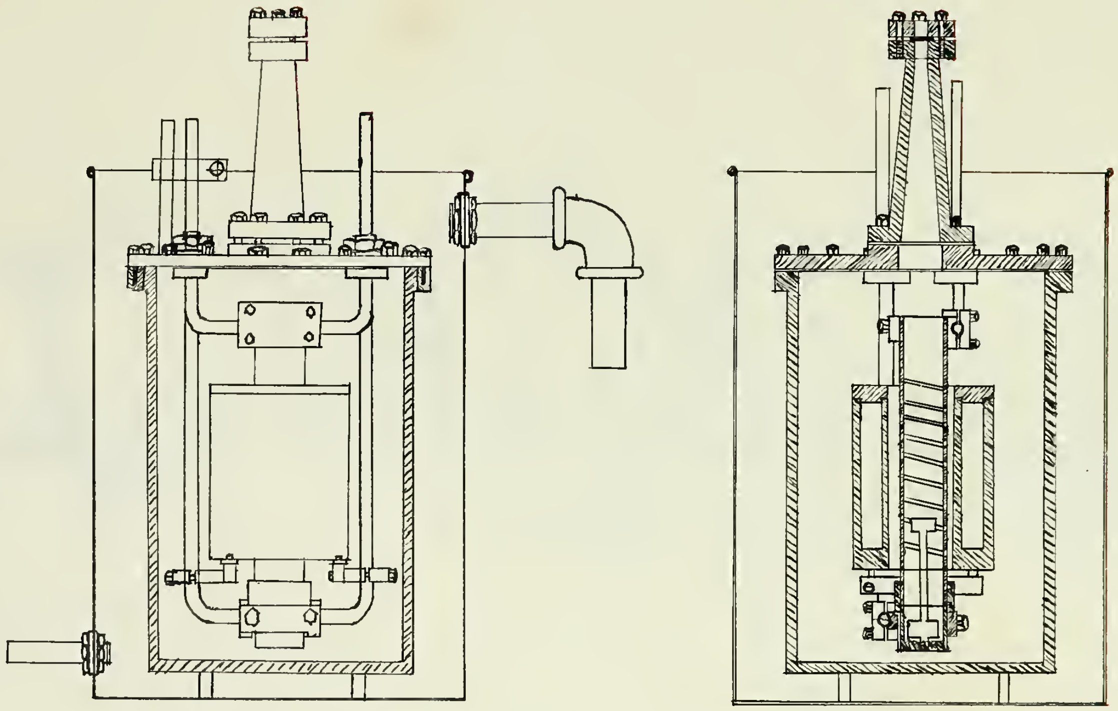

Fig. 1
Assembly Electric Vacuum Furnace

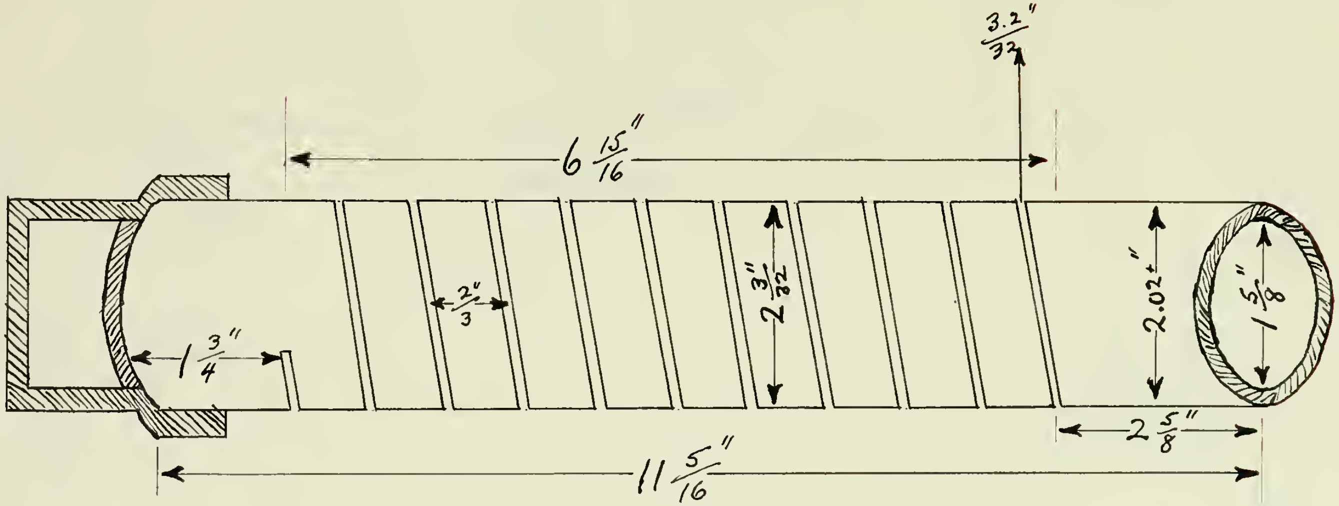

Fig. 2
Drawing of Helix

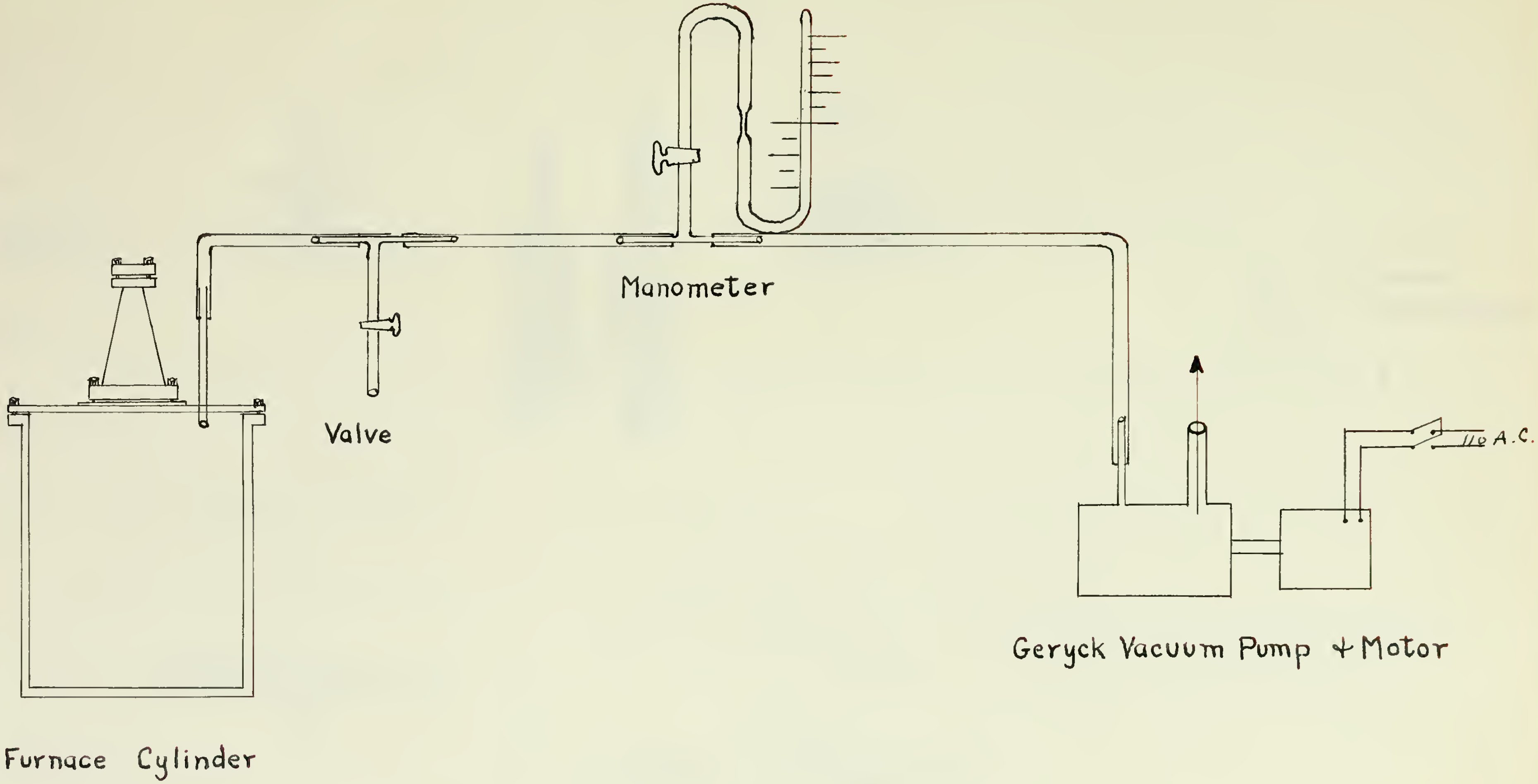
Manometer
Valve
110 A.C.
Geryck Vacuum Pump + Motor
Furnace Cylinder

Fig. 3

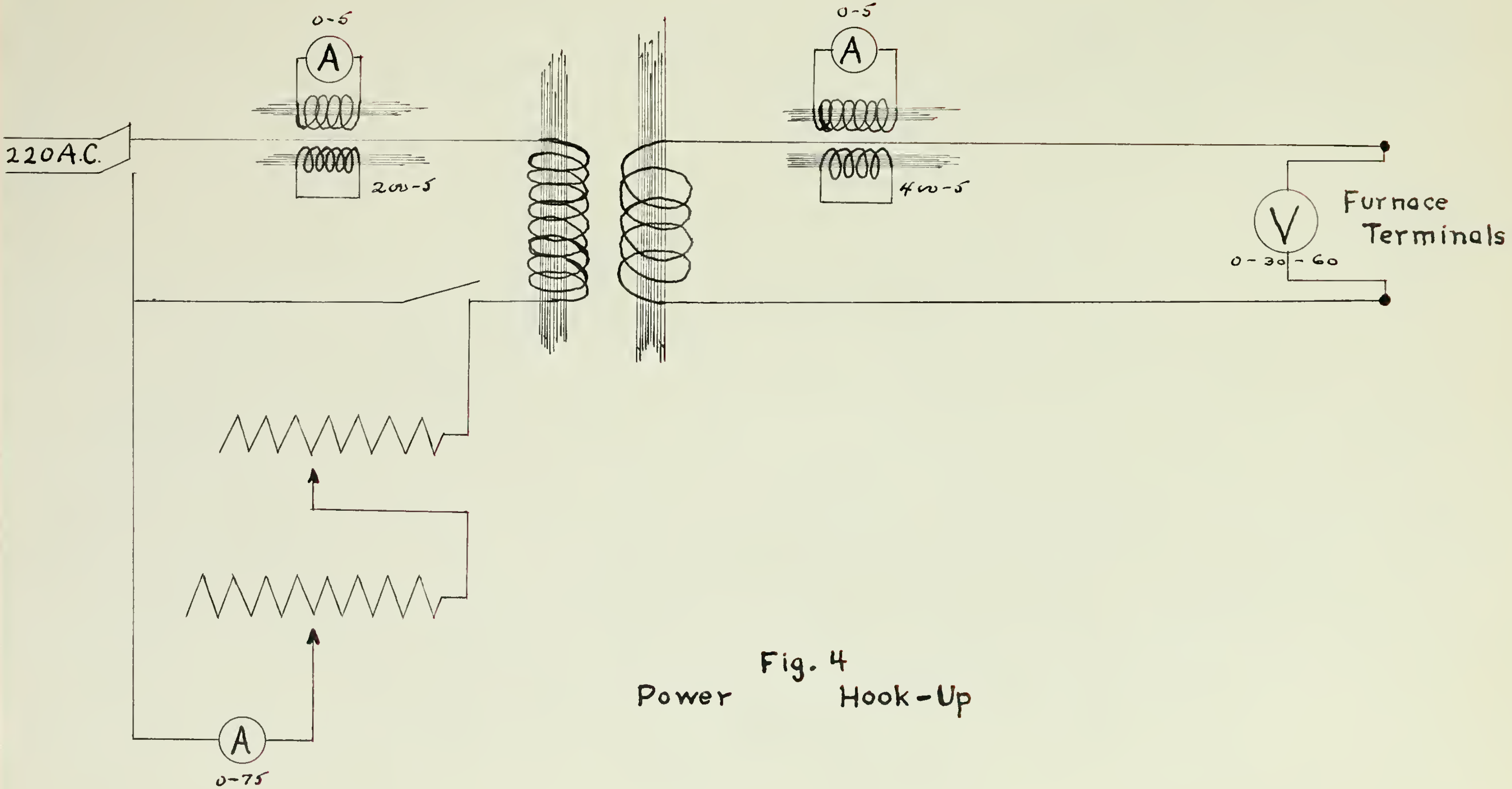

Fig. 4
Power Hook-Up

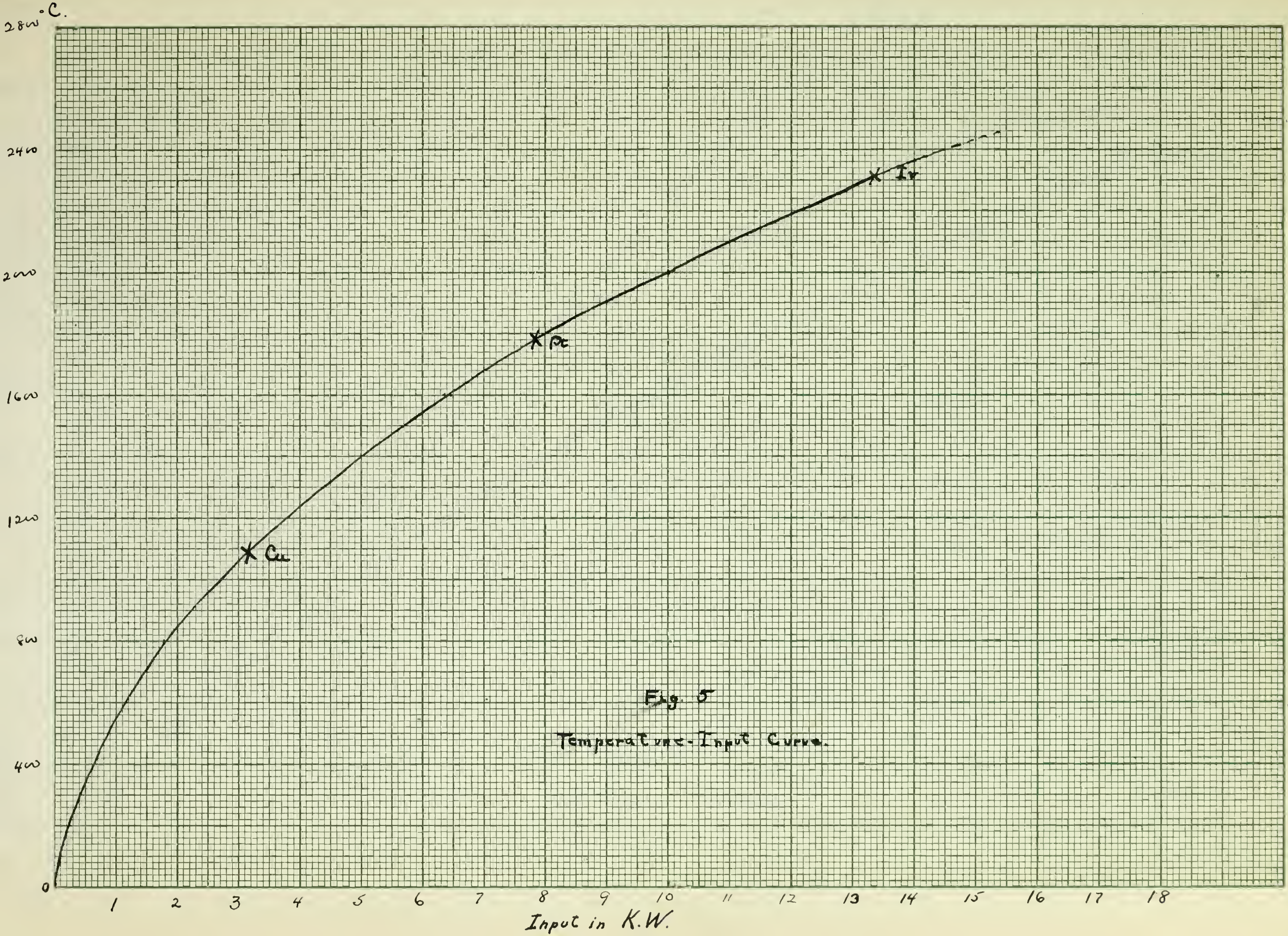

Fig. 5

Temperature-Input Curve.

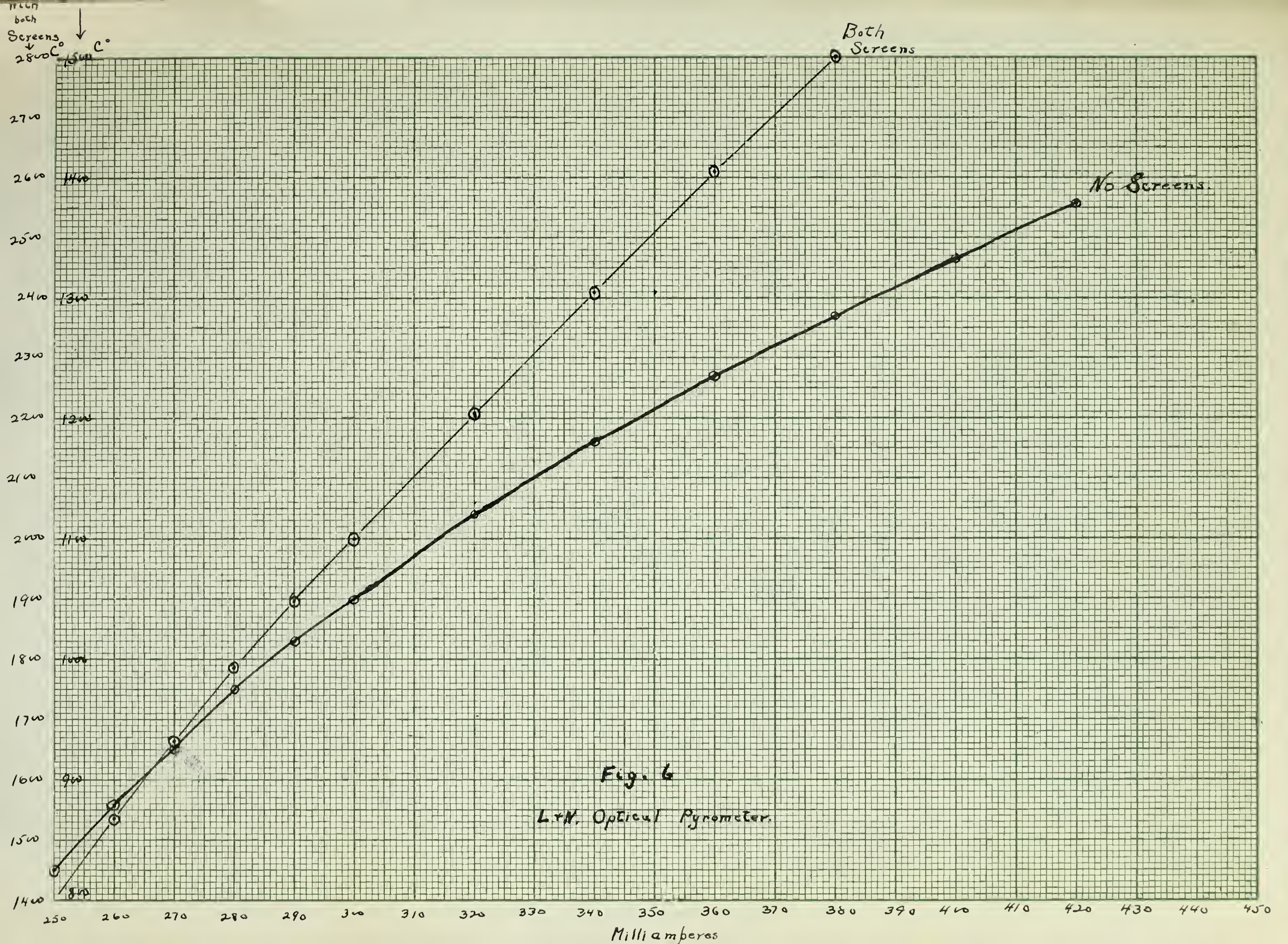

Fig. 6

L+N. Optical Pyrometer.